STUDIES ON SYNTHESIS, CHARACTERIZATION, CRYSTAL GROWTH AND NON-LINEAR OPTICAL PROPERTY OF CHALCONE AND CYCLOHEXENONE DERIVATIVES

SYNOPSIS

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STUDIES ON SYNTHESIS, CHARACTERIZATION, CRYSTAL GROWTH AND NON-LINEAR OPTICAL PROPERTY OF CHALCONE AND CYCLOHEXENONE DERIVATIVES

Synopsis of the Ph.D. Thesis of Ms. Rashmi M to be submitted for the award of Ph.D. degree under the Guidance of Dr. Indira. J., Research Guide, Department of Physics, University College Mangalore- 575001, and Prof. B.K. Sarojini, Research Co-guide, Department of Industrial Chemistry, Mangalore University, Mangalagangothri-574199)

Introduction:

Nonlinear optical (NLO) materials have a significant impact on the field of nonlinear optics and are very relevant for industrial and information technology applications. The goal is to develop materials with large nonlinearities that concurrently satisfy all application-specific technological requirements, such as a high damage threshold, rapid reaction times, and a wide transparency range. The important characteristic of NLO organic materials is the conjugated interaction between an acceptor group and a donor group on opposite sides. Chalcone derivatives exhibit strong absorption in the visible and/or ultraviolet spectrum, notable optical nonlinearities with fast response, including absorption of two photons, and good crystallizability. These derivatives are appropriate nonlinear optical materials due to their larger optical band gap. These chalcone derivative materials have an intensity-dependent refractive index and a significant absorption coefficient, which makes them useful for optical device applications. Likewise, the wide range of optical characteristics and chemical versatility of cyclohexenone derivatives makes them desirable compounds for organic light-emitting devices. The objective of this research is to synthesise chalcone

derivatives and cyclohexenone carboxylate derivatives, growing single crystals, and to characterise them using linear and non-linear optical studies.

The thesis entitled "Studies on synthesis, characterization, crystal growth and non-linear optical property of chalcone and cyclohexenone derivatives" has been divided into five chapters.

Objectives of research work:

- To synthesis chalcone derivatives **A**-series and cyclohexenone derivatives **B**-series compounds with the help of Claisen-Schimdt condensation method and Micheal addition reaction
- To characterize the organic crystals by spectroscopic and single crystal XRD study
- To determine optical band gap by linear optical activity of chalcone & cyclohexenone derivatives
- To determine SHG property of organic molecules
- To study third order nonlinear optical properties of the organic molecules using Z-scan spectroscopy

CHAPTER 1: REVIEW ON RECENT DEVELOPMENT IN OPTICAL STUDIES IN THE AREA OF CHALCONE DERIVATIVES AND CYCLOHEXENONE CARBOXYLATE DERIVATIVES

This chapter affords a concise overview of the latest advancements in the field of optical studies concerning chalcone derivatives and cyclohexenone carboxylate derivatives.

Organic compounds are important in many areas, including data storage, optical storage, micro fabrication, imaging, laser technology, communications, luminous materials, and organic sensors and switches [1]. Having high nonlinear optical (NLO) qualities sets organic materials apart from other materials [2-5]. In response to an electric field, compounds with a π-electron system are mostly affected by second order NLO effects. A great deal of research has been done on nonlinear optical organic materials in an attempt to identify materials with significant and rapid optical nonlinearities. Second order hyperpolarizability of the compound is proportional to changes in the dipole moment, the energy difference between the ground and excited

states, and the intensity of the excited state transition [6]. Organic materials exhibiting significant third order nonlinearities exhibit nonlinear transmission as well as intensity-dependent variations in their refractive index.

Chalcone derivative compounds

Chalcone derivatives are an interesting group of materials because of their good crystallizability and high NLO coefficients [7]. It is possible to synthesise novel compounds that replace donor or acceptor groups owing to the intramolecular charge-transfer feature of chalcone derivatives, which provides insight into the structure-property relationship. Several chalcone materials containing two planar benzene rings joined by a conjugated double bond and a carbonyl moiety are reported to crystallise in a noncentrosymmetric crystal pattern, offering the required configuration for NLO activity [8]. These systems exhibit extraordinary third order nonlinearities and high molecule polarizability due to substantial delocalization of π- electrons. Through structural alteration, they can be made to respond ultra-fast and with great nonlinearity [9]. These materials are helpful for optical device applications because of their large absorption coefficient and intensity-dependent refractive index.

Cyclohexenone carboxylate derivative compounds

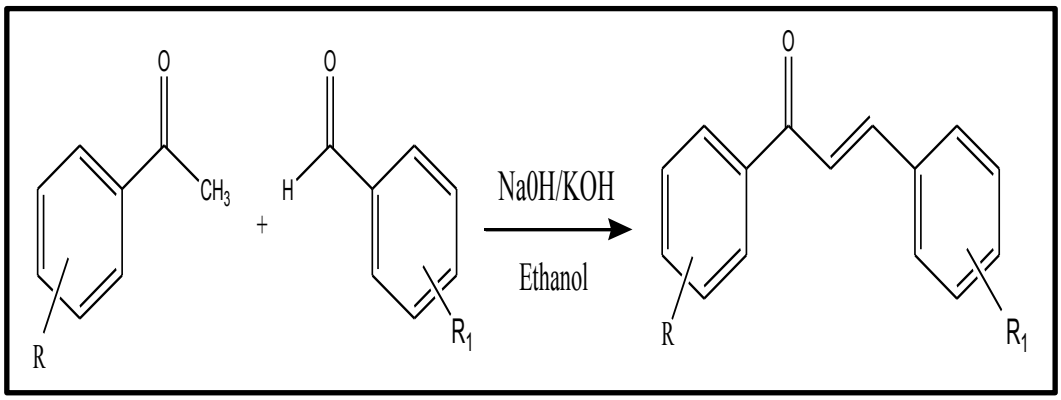
Good nonlinearity properties have been demonstrated by the cyclohexenone carboxylate derivative compounds. Higher optical thresholds and larger optical susceptibilities have drawn a lot of attention on these compounds. The rapid response times of the compound are intrinsic [10]. NLO response of the carboxylate compounds obtained through conjugated bridge extension and/or donor-acceptor strength optimisation. Compounds derived from cyclohexene are commonly employed in light-emitting devices.

CHAPTER 2: METHODS OF SYNTHESIS AND CHARACTERIZATION TECHNIQUES

Synthesis of chalcone derivative compounds

Chalcone derivative compounds were synthesised by Claisen–Scmidt condensation method [11]. This reaction is carried out of substituted acetophenone with substituted benzaldehyde in the presence of alkali [8]. Based on the **Scheme 2.1**, chalcone

derivative compounds were synthesised. After getting the precipitate, using ice cold water sample is filtered in a buckle funnel. The obtained sample is dried and recrystallized. For recrystallization, different solvents like acetone, ethanol, methanol are used.

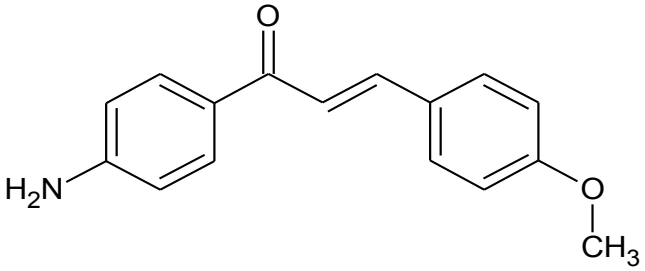
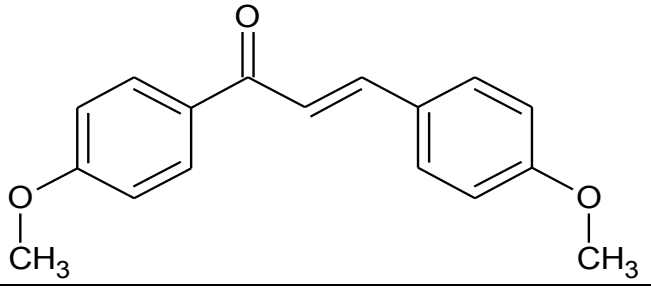


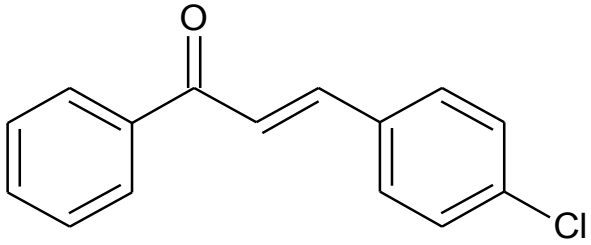
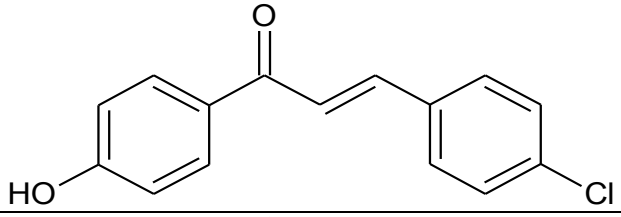
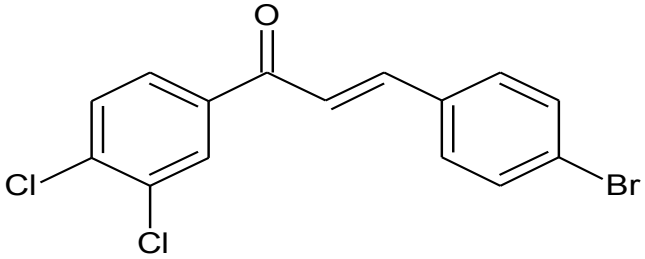
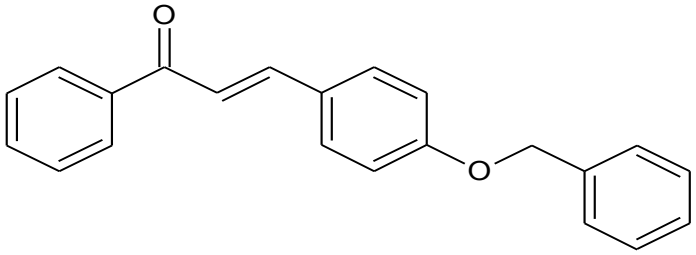
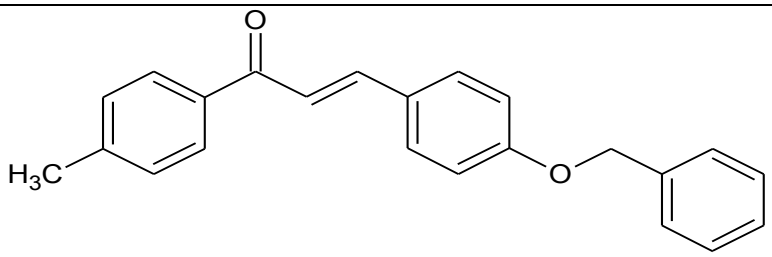
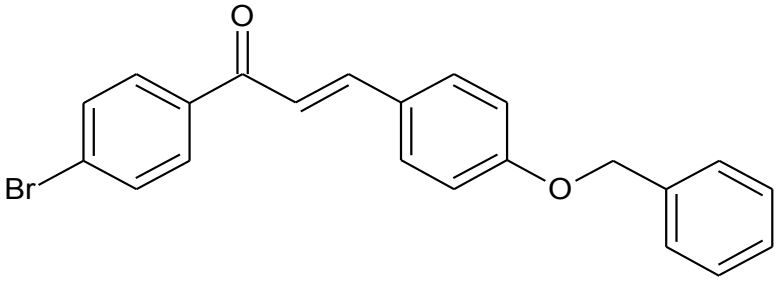
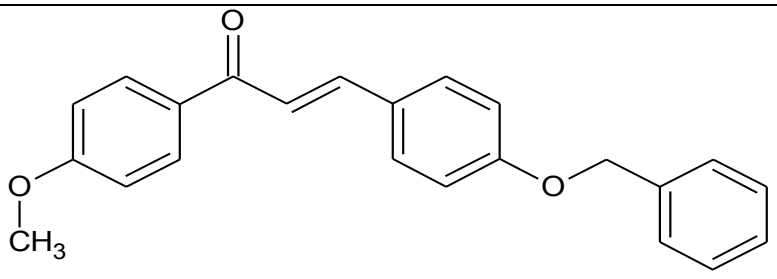
Scheme 2.1: Preparation of chalcone derivatives

R = H_2N, OCH_3, OH, Cl_2, CH_3, Br

R_1= OCH_3, Cl, Br, OC_7H_7

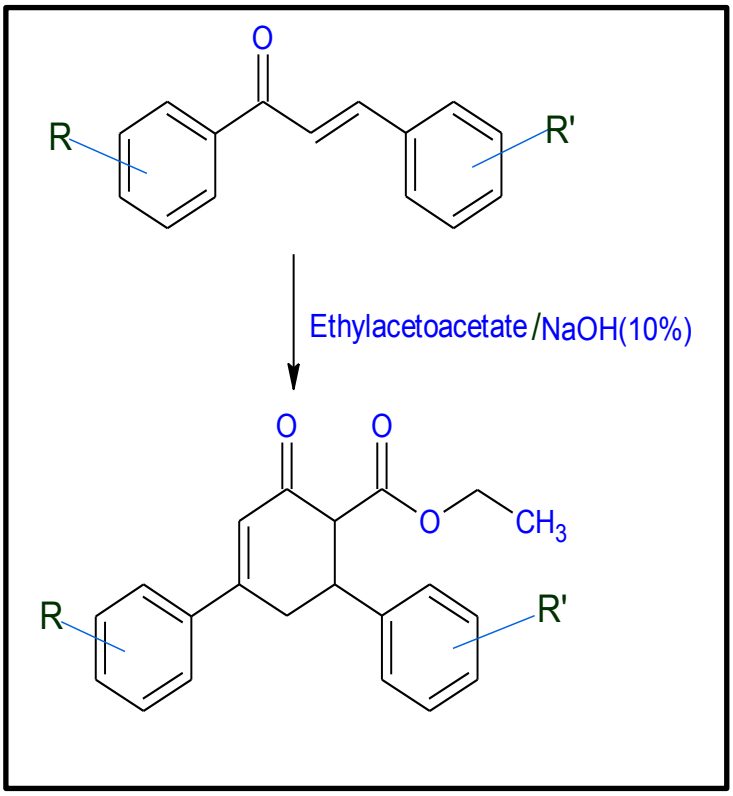
Based on the above scheme, the following A-series chalcone derivative compounds were synthesised.

Compound	Structure of the Compound
A1	
A2	

A3	
A4	
A5	
A6	
A7	
A8	
A9	

Synthesis of cyclohexenone carboxylate derivatives

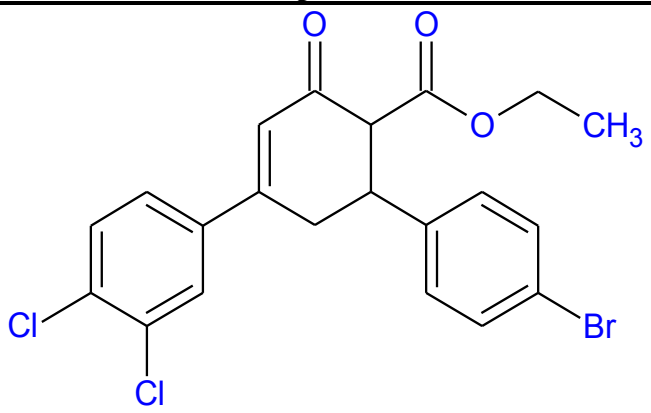
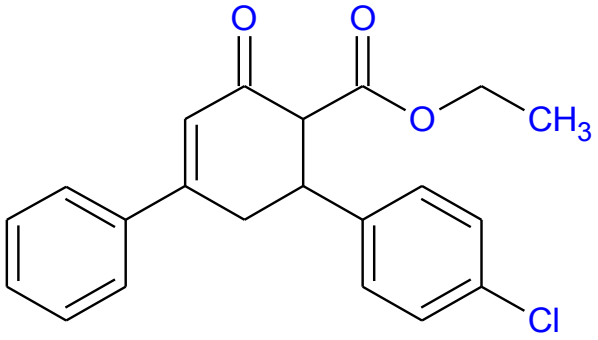
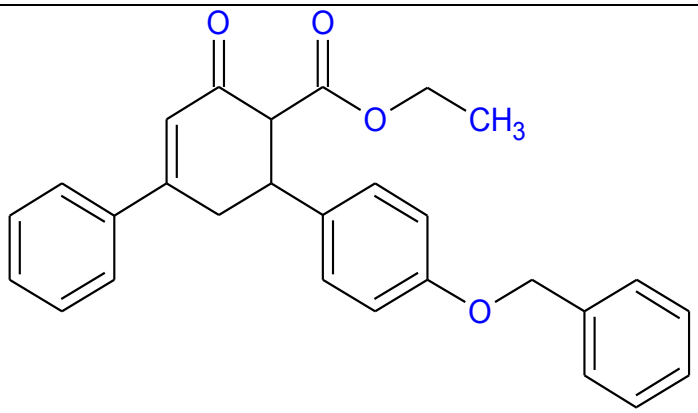
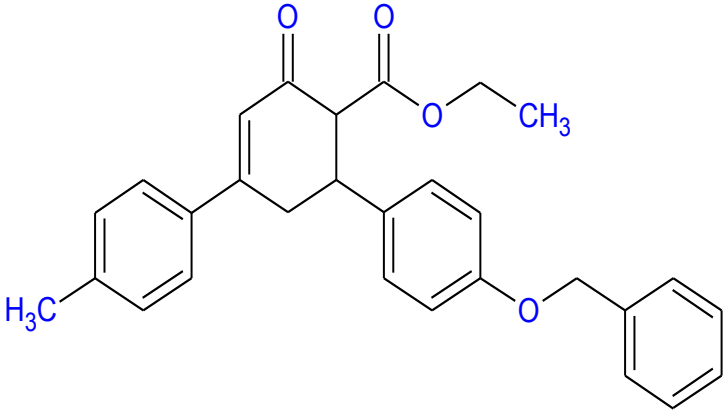
The A-series (A1-A9) chalcone derivatives were subjected to a Michael addition reaction to obtain cyclohexenone carboxylate derivatives [12]. The A-series compounds (0.001 mol) and ethylacetoacetate (0.001mol) were refluxed for 8 to 10 hrs in 20 ml of ethanol and 0.8 ml of 10% sodium hydroxide (NaOH). At the bottom of round bottom flask, precipitate was observed and the flask was kept in a cold water bath. Once the mixture was cooled, precipitate was collected by filtration and dried. The general scheme for the synthesis of carboxylate compounds is given below **Scheme 2.2.**

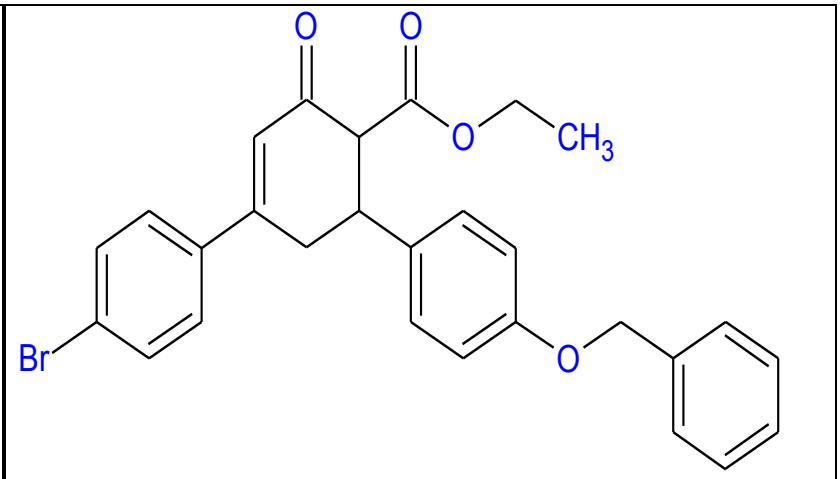
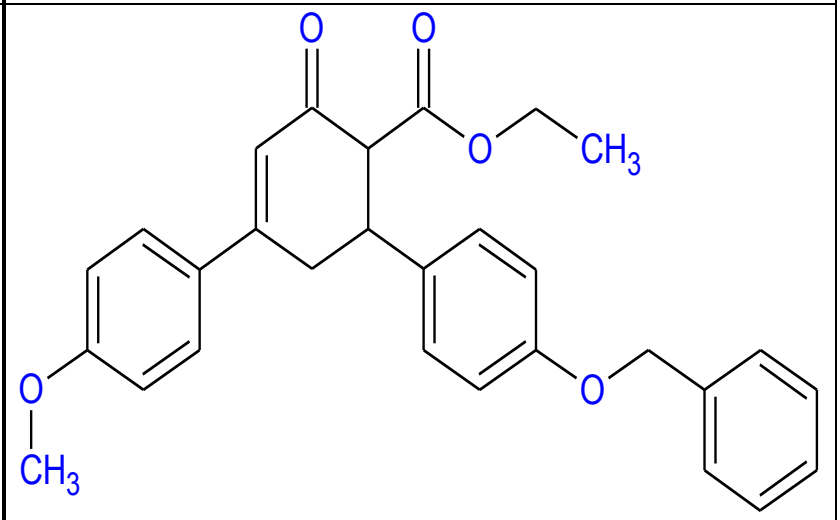


Scheme 2.2: Synthesis and reaction scheme of carboxylate compounds

R= H, 2,3-dichloro, 4-bromo,4-methyl,4-methoxy
R'= 4- Chloro, 4-bromo, 4-benzyloxy

Based on the above scheme, B-series cyclohexenone carboxylate derivatives were synthesised.

Compound	Structure of the Compound
B1	
B2	
B3	
B4	

B5	
B6	

In this chapter, the specific experimental methods used to carry out the synthesis of the molecules used in this research work. It also contains basic details about each of these organic compounds. Additionally, characterisation technique details carried out in this study.

CHAPTER 3: CRYSTAL GROWTH, SINGLE CRYSTALS OF CHALCONE DERIVATIVES

In this chapter, the growths of single crystals are discussed based on the single crystal X–ray diffraction studies. It is a highly effective method utilised to gather comprehensive information on the three-dimensional configuration of crystals. Modern optical and electronic technology is built on the principle of the single

crystals. Single crystals of the chalcone derivative and cyclohexenone carboxylate derivatives were grown using slow evaporation technique.

CHAPTER 4: LINEAR AND NON-LINEAR OPTICAL STUDIES ON CHALCONE DERIVATIVES

In this chapter, Claisen-Schmidt condensation method was utilised to synthesise chemicals that are derivatives of chalcone **A**-series. Re-crystallization was used to purify the resulting chemicals at room temperature. Studies on the ultraviolet (UV) and density functional theory (DFT) were used to characterise the optical properties of these derivatives. The third order nonlinear experiments were conducted utilising the *Z*-scan open and closed aperture approach. While derivatives **A7** and **A8** show a reverse saturable absorption (RSA), derivative **A6** shows a saturable absorption (SA). The chalcone derivatives were observed to exhibit self-focusing behaviour. Regarding photonic applications, the A-series derivative compounds are the promising materials.

CHAPTER 5: LINEAR AND NON-LINEAR OPTICAL STUDIES ON CYCLOHEXENONE CARBOXYLATE DERIVATIVES

In this chapter, **B**-series carboxylate derivatives **B1**, **B2**, **B3**, **B4**, **B5** and **B6** were synthesized by Michael addition reaction. For **B1**, **B2**, **B3**, **B4**, **B5**, and **B6**, the corresponding UV absorption λ_{max} values were found to be 288, 287, 284, 296, 292, and 319 nm. Likewise, HOMO-LUMO was utilised to compute the optical band gap of these carboxylate compounds. . The nonlinear absorption (NLA) coefficient, β value of these compounds were found as $1.028X10^{-12}$, $-3.89x10^{-12}$, $-4.23x10^{-12}$, $-3.71x10^{-12}$, $-3.30x10^{-12}$ m/W and nonlinear refractive (NLR) index, n_2 were determined as $8.44x10^{-19}$, $16.83x10^{-19}$, $13.87x10^{-19}$, $6.11x10^{-19}$, $6.86x10^{-19}$ m^2/W. Third order nonlinear susceptibility, $\chi^{(3)}$ were found as $3.62\ x10^{-13}$, $12.29x10^{-13}$, $7.8x10^{-13}$, $4.16x10^{-13}$, $4.85x10^{-13}$, esu. From the open aperture data of the z-scan investigation, the carboxylate compounds were seen to be saturable absorbers with a negative NLA coefficient. This observation may be related to the compounds greater band gap values, which are caused by their nonpolarizable form. Despite having prolonged conjugation, the envelop structure of cyclohexenone derivatives led to nonpolarizability.

Outcome of the work

- Chalcone derivative **A**-series compounds were synthesised by Claisen–Scmidt condensation method
- **A**-series chalcone derivatives undergoes Michael addition reaction and **B**-series cyclohexenone carboxylate compounds were synthesised
- Compounds **A1**, **A3**, and **A8** have demonstrated second order nonlinear optical study
- Third order nonlinear optical investigation has been demonstrated by Compounds **A6**, and **A7** because of their centrosymmetric character
- Compound **A6** exhibits saturable absorption, but compounds **A7** and **A8** exhibit reverse saturable absorption due to the presence of methyl and bromine as replacement groups
- Higher optical band gaps were observed in cyclohexenone carboxylate compounds which has led to the nonpolarizability nature due to envelop conformations of cyclohexene ring avoiding delocalization
- Among the other derivatives, **B3** has the highest nonlinear refractive index (16.83×10^{-19} m^2/W) and nonlinear susceptibility (12.29×10^{-13}esu), suggesting that substitution by an acceptor or donor of electrons lowers the susceptibilities
- These saturable absorbers could find use in Q-switching, laser cavities, mode locking devices, etc. These organic compounds NLO property are best suitable for its application in opto-electronic devices

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List of Publications

1. **M. Rashmi**, J. Indira, B. K. Sarojini, B. J. Mohan, I. H. Joe, P. Aswathy, "Ultrafast nonlinear optical properties of cyclohexenone carboxylate derivatives and their application as organic saturable absorbers", **Optics & Laser Technology**, 2021 Jul 1, Vol. 139, 106902; https://doi.org/10.1016/j.optlastec.2020.106902.
2. **M. Rashmi**, Indira J, Sarojini B. K., Harshitha K. R., Synthesis of (2*E*)-3-(4-bromophenyl)-1-(3, 4-dichlorophenyl) prop-2-en-1-one and characterization, In **AIP Conference Proceedings** 2020 Jun 26, Vol. 2244, No. 1, p. 060004; https://doi.org/10.1063/5.0009478.
3. **M. Rashmi**, J. Indira, B. K. Sarojini, K. R. Harshitha, "Synthesis and SHG studies on D-π-D type chalcone derivative for optoelectronic application", **Proceedings of NCASEM-2019**, ISBN: 978-81-934215-3-6, **2019**, pp.: 345-347.

Paper presented in National/ International Conferences

1. National Conference on "Advances in Science, Engineering and Management", organized by Vivekananda College of Engineering and Technology, Puttur on 23rd -24th August 2019, **ORAL PRESENTATION**, **Topic**: Synthesis and SHG studies on D-π-D type chalcone derivative for optoelectronic application.
2. International conference on "Physics of Materials & Nanotechnology (ICPN-2019)", organized by Mangalore University, Mangalagangothri on 19th - 21st September 2019, **POSTER PRESENTATION**, **Topic:** Synthesis of (2*E*)-3-(4-bromophenyl)-1-(3,4-dichlorophenyl)prop-2-en-1-one And Characterization.
3. International conference on "Advances in Chemical and Materials Sciences (ICCM- 2019)", organized by Mangalore University, Mangalagangothri on 17th – 19th October 2019, **POSTER PRESENTATION**, **Topic:** Effect of Bandgap Energy on SHG response in Bischalcone derivatives.

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